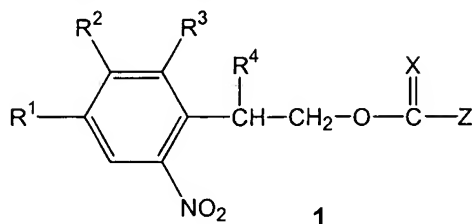


## CLAIMS

1. A compound having the general formula (1):



wherein

$R^1$  is COOY, wherein Y is selected from the group consisting of an optionally substituted alkyl group of up to 10 carbon atoms, under the proviso that  $R^2$  is selected from the group consisting of H, NO<sub>2</sub>, CN, OCH<sub>3</sub> or halogen or is an optionally substituted alkyl or alkoxy group, respectively, having up to 4 carbon atoms; or

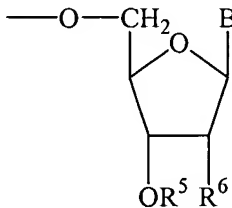
$R^1$  is selected from the group consisting of H, NO<sub>2</sub>, CN, OCH<sub>3</sub> or halogen or an optionally substituted alkyl or alkoxy group respectively, having up to 4 carbon atoms, under the proviso that  $R^2$  is selected from the group consisting of an optionally substituted aryl group, an optionally substituted heteroaryl group or an optionally substituted aroyl group;

$R^3$  is selected from the group consisting of H, NO<sub>2</sub> or halogen;

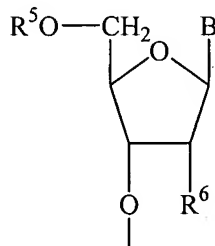
$R^4$  is selected from the group consisting of H, OCH<sub>3</sub> or an optionally substituted alkyl group having up to 4 carbon atoms;

X is selected from oxygen or sulfur; and

Z is selected from the group consisting of a leaving group, a primary or secondary amine, an alcohol, or a deoxyribonucleoside or ribonucleoside as represented by either of the following formulae (2) or (3):



2



3

wherein

$R^5$  is selected from the group consisting of a H, an oligonucleotide or a functional group useful in oligonucleotide synthesis;

R<sup>6</sup> is selected from the group consisting of H, OH or an optionally substituted alkoxyl or alkenoxyl group respectively, having up to 4 carbon atoms, or WR<sup>8</sup> wherein W is selected from oxygen and sulfur and R<sup>8</sup> is selected from a protective group useful in oligonucleotide synthesis;

5 B is a purine or pyrimidine base selected from the group consisting of adenine, cytosine, guanine, thymine, uracil or chemical modifications thereof and in the case of adenosine, cytosine and guanine the amino functions on the heterocycle may bear a protective group useful in oligonucleotide synthesis; or

10 Z is selected from the group consisting of a chemically modified deoxyribonucleoside or ribonucleoside, or an analog thereof.

2. The compound of claim 1, wherein Y is an alkyl group selected from the group consisting of methyl or tertiary-butyl, and R<sup>2</sup> is H.

15 3. The compound of claim 1, wherein R<sup>1</sup> is H and R<sup>2</sup> is an optionally substituted phenyl.

4. The compound of claim 1, wherein R<sup>1</sup> is H and R<sup>2</sup> is an optionally substituted benzoyl.

20 5. The compound of claim 1 wherein W is O and R<sup>8</sup> is selected from the group consisting of an alkyl, alkenyl, acetal or silylether protective group.

25 6. The compound of claim 1 wherein W is S and R<sup>8</sup> is selected from the group consisting of an alkyl protective group.

7. The compound of claim 1, wherein R<sup>6</sup> is selected from the group consisting of an O-methyl, O-ethyl, O-allyl, O-tetrahydropyranyl- O-methoxytetrahydropyranyl or an O-t-butyl dimethylsilyl.

8. The compound of claim 1, wherein B is selected from the group consisting of adenine, cytosine or guanine and said protective group is selected from the group consisting of phenoxyacetyl, 4-tert-butyl-phenoxyacetyl, 4-isopropyl-phenoxyacetyl or dimethylformamidino.

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9. The compound of claim 8, wherein B is adenine and the protective group is selected from the consisting of benzoyl or p-nitrophenyloxycarbonyl (p-NPEOC).

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10. The compound of claim 8, wherein B is guanine and the protective group is selected from the group consisting of isobutyroyl or p-nitrophenylethyloxycarbonyl (p-NPEOC).

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11. The compound of claim 8, wherein B is cytosine and the protective group is selected from the group consisting of benzoyl, t isobutyroyl or p-nitrophenylethyl-oxycarbonyl (p-NPEOC).

12. The compound of claim 1, wherein  $R^5$  is a phosphitamide group.

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13. The compound of claim 1, wherein  $R^5$  is selected from an intermediate OH-protective group.

14. The compound of claim 13, wherein  $R^5$  is selected from a dimethoxytrityl- or a monomethoxytrityl- group.

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15. The compound of claim 13, wherein  $R^5$  is a silyl-group.

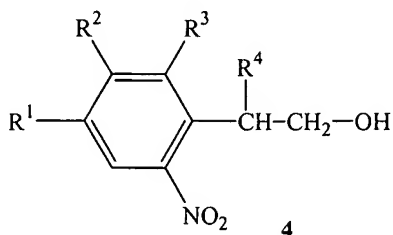
16. The compound of claims 1, 2, 3 or 4, wherein Z is selected from a leaving group.

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17. The compound of claim 16, wherein the leaving group is selected from the group consisting of chloride, imidazolyl or nitrophenoxyl.

18. A method for the preparation of a derivatized nucleoside or nucleoside analog thereof comprising the steps of:

a) reacting an alcohol having the general formula 4:



wherein

R<sup>1</sup> is COOY, wherein Y is selected from the group consisting of an optionally substituted alkyl group of up to 10 carbon atoms, under the proviso that R<sup>2</sup> is selected from the group consisting of H, NO<sub>2</sub>, CN, OCH<sub>3</sub>, halogen or an optionally substituted alkyl or alkoxy group, respectively, having up to 4 carbon atoms; or

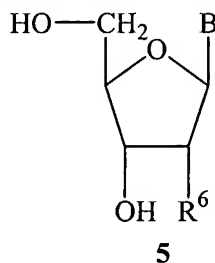
R<sup>1</sup> is selected from the group consisting of H, NO<sub>2</sub>, CN OCH<sub>3</sub> or halogen or an optionally substituted alkyl or alkoxy group respectively, having up to 4 carbon atoms, under the proviso that R<sup>2</sup> is selected from the group consisting of an optionally substituted aryl group, an optionally substituted heteroaryl group or an optionally substituted aroyl group;

R<sup>3</sup> is selected from the group consisting of H, NO<sub>2</sub> or halogen; and

R<sup>4</sup> is selected from the group consisting of H, OCH<sub>3</sub> or an optionally substituted alkyl group having up to 4 carbon atoms;

with phosgene or a derivative or substitute thereof, or with the respective thiocarbonyl compound, to produce an activated carbonate ester or thiocarbonate ester and

b) reacting the activated carbonate or thiocarbonate ester as formed in step a) with a nucleoside selected from the group consisting of compounds having the general formula (5):

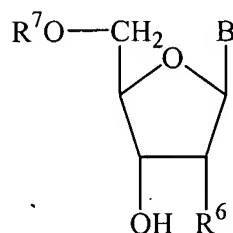


wherein

$R^6$  is selected from the group consisting of H, OH or an optionally substituted alkoxy or alkenoxy group respectively, having up to 4 carbon atoms, or  $WR^8$  wherein W is selected from oxygen or sulfur and  $R^8$  is selected from a protective group useful in oligonucleotide synthesis and

5 B is a purine or pyrimidine base selected from the group consisting of adenine, cytosine, guanine, thymine, uracil or chemical modifications thereof and in the case of adenosine, cytosine and guanine the amino functions on the heterocycle may optionally bear a protective group useful in oligonucleotide synthesis; or with a nucleosidic derivative or analog comprising an unprotected primary hydroxyl function;

10 or with a nucleoside selected from the group of compounds having general formula (6):



wherein

15  $R^6$  is selected from the group consisting of H, OH or an optionally substituted alkoxy or alkenoxy group respectively, having up to 4 carbon atoms, or  $WR^8$  wherein W is selected from oxygen or sulfur and  $R^8$  is selected from a protective group useful in oligonucleotide synthesis and

20  $R^7$  is selected from an intermediate protective group or selected from the group of nucleosidic and nucleotidic derivatives as well as analogs thereof accordingly comprising an intermediately protected primary hydroxyl;

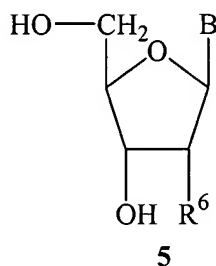
c) optionally removing the intermediate protective group and purifying the product; and

d) reacting the product from step b) or c) with a phosphitylation reagent to provide after purification a phosphoramidite.

25 19. The method of claim 18 wherein said phosphitylation reagent is bis(diisopropylamino)- $\beta$ -cyanoethoxy phosphane.

20. A method for the preparation of a derivatized nucleoside or nucleoside analog thereof comprising the steps of:

a) reacting a nucleoside selected from the group consisting of compounds having the general formula (5):



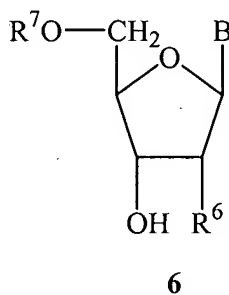
wherein

$R^6$  is selected from the group consisting of H, OH or an optionally substituted alkoxy or alkenoxy group respectively, having up to 4 carbon atoms, or  $WR^8$  wherein W is selected from oxygen or sulfur and  $R^8$  is selected from a protective group useful in oligonucleotide synthesis and

B is a purine or pyrimidine base selected from the group consisting of adenine, cytosine, guanine, thymine, uracil or chemical modifications thereof and in the case of adenosine, cytosine and guanine the amino functions on the heterocycle may optionally bear a protective group useful in oligonucleotide synthesis;

or reacting a nucleosidic derivative or analog comprising an unprotected primary hydroxyl function;

or reacting a nucleoside selected from the group of compounds having general formula (6):



wherein

$R^6$  is selected from the group consisting of H, OH or an optionally substituted alkoxy or alkenoxy group respectively, having up to 4 carbon atoms, or  $WR^8$  wherein W is selected

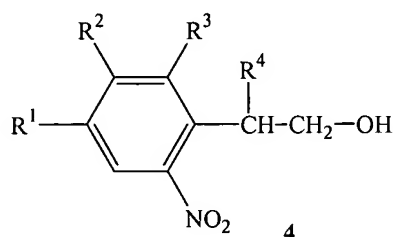
from oxygen or sulfur and R<sup>8</sup> is selected from a protective group useful in oligonucleotide synthesis and

R<sup>7</sup> is selected from an intermediate protective group or selected from the group of nucleosidic and nucleotidic derivatives as well as analogs thereof accordingly comprising an  
5 intermediately protected primary hydroxyl function;

or reacting a nucleosidic derivative or analog comprising an unprotected secondary hydroxyl function;

with phosgene or a derivative or substitute thereof, or with the respective thiocarbonyl compound, to produce an activated carbonate ester or thiocarbonate ester;

10 b) reacting the activated carbonate or thiocarbonate ester as formed in step a) with an alcohol having the general formula 4:



wherein

R<sup>1</sup> is COOY, wherein Y is selected from the group consisting of an optionally  
15 substituted alkyl group of up to 10 carbon atoms, under the proviso that R<sup>2</sup> is selected from the group consisting of H, NO<sub>2</sub>, CN, OCH<sub>3</sub>, halogen or an optionally substituted alkyl or alkoxy group, respectively, having up to 4 carbon atoms; or

R<sup>1</sup> is selected from the group consisting of H, NO<sub>2</sub>, CN OCH<sub>3</sub> or halogen or an optionally substituted alkyl or alkoxy group respectively, having up to 4 carbon atoms, under  
20 the proviso that R<sup>2</sup> is selected from the group consisting of an optionally substituted aryl group, an optionally substituted heteroaryl group or an optionally substituted aroyl group;

R<sup>3</sup> is selected from the group consisting of H, NO<sub>2</sub> or halogen; and

R<sup>4</sup> is selected from the group consisting of H, OCH<sub>3</sub> or an optionally substituted alkyl group having up to 4 carbon atoms;

25 c) optionally removing the intermediate protective group and purifying the product; and

d) reacting the product from step b) or c) with a phosphitylation reagent to provide after purification a phosphoramidite.

21. The method of claim 20 wherein said phosphitylation reagent is bis(diisopropylamino)- $\beta$ -cyanoethoxy phosphane.

5 22. A method for the light-controlled synthesis of oligonucleotides employing phosphoramidites of claim 12.

23. The method of claim 21, wherein the light controlled oligonucleotide synthesis is effected on a solid support.

10 24. A method for the light-controlled synthesis of oligonucleotides, wherein said method is comprised of the following steps:

a) attaching a first nucleotide having a secondary (3') hydroxyl group and a primary (5') hydroxyl group to a support via its secondary (3') hydroxyl group, wherein said  
15 5' hydroxyl group is derivatized with an inventive protective group;

b) irradiating the support-bound nucleotide resulting from step a), such that the 5' protective group is removed, thereby deprotecting the 5' hydroxyl group;

c) reacting the support-bound nucleotide resulting from step b) in the presence of an activator with a second nucleotide selected from the claim 12 comprising a 5' protective  
20 group and a 3' phosphoramidite functional group, to form an internucleosidic phosphorous linkage;

d) optionally capping unreacted 5'-hydroxyl groups with an inert alcohol protecting group;

25 e) oxidizing the internucleosidic phosphorous linkage to the naturally occurring pentavalent state;

f) iterating steps b) to d) while successively applying the phosphoramidites in a predetermined order until the desired oligonucleotide strand is completed; and

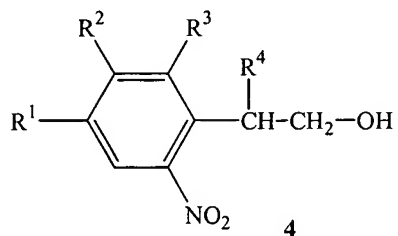
g) removing of all nucleobase and phosphate protective groups.

30 25. A method for the light-controlled synthesis of oligonucleotides, wherein said method is comprised of the following steps:



- a) attaching a first nucleotide having a secondary (3') hydroxyl group and a primary (5') hydroxyl group to a support via its primary (5') hydroxyl group, wherein said 3' hydroxyl group is derivatized with an inventive protective group;
- b) irradiating the support-bound nucleotide resulting from step a), such that the 3' protective group is removed, thereby deprotecting the 3' hydroxyl group;
- c) reacting the support-bound nucleotide resulting from step b) in the presence of an activator with a second nucleotide selected from the claim 12 comprising a 3' protective group and a 5' phosphoramidite functional group, to form an internucleosidic phosphorous linkage;
- d) optionally capping unreacted 3'-hydroxyl groups with an inert alcohol protecting group;
- e) oxidizing the internucleosidic phosphorous linkage to the naturally occurring pentavalent state;
- f) iterating steps b) to d) while successively applying the phosphoramidites in a predetermined order until the desired oligonucleotide strand is completed; and
- g) removing of all nucleobase and phosphate protective groups.

26. A compound having the following general formula:



wherein

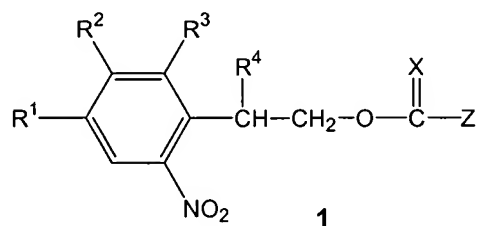
$R^1$  is COOY, wherein Y is selected from the group consisting of an optionally substituted alkyl group of up to 10 carbon atoms, under the proviso that  $R^2$  is selected from the group consisting of H, NO<sub>2</sub>, CN, OCH<sub>3</sub>, halogen or an optionally substituted alkyl or alkoxy group, respectively, having up to 4 carbon atoms; or

$R^1$  is selected from the group consisting of H, NO<sub>2</sub>, CN, OCH<sub>3</sub> or halogen or an optionally substituted alkyl or alkoxy group respectively, having up to 4 carbon atoms, under the proviso that  $R^2$  is selected from the group consisting of an optionally substituted aryl group, an optionally substituted heteroaryl group or an optionally substituted aroyl group;

$R^3$  is selected from the group consisting of H,  $\text{NO}_2$  or halogen; and

$R^4$  is selected from the group consisting of H,  $\text{OCH}_3$  or an optionally substituted alkyl group having up to 4 carbon atoms.

27. A method for derivatizing a compound having a primary amine, a secondary amine or a hydroxyl group said method comprising the step of reacting said compound with a compound having the general formula:



wherein

$R^1$  is  $\text{COOY}$ , wherein Y is selected from the group consisting of an optionally substituted alkyl group of up to 10 carbon atoms, under the proviso that  $R^2$  is selected from the group consisting of H,  $\text{NO}_2$ , CN,  $\text{OCH}_3$  or halogen or is an optionally substituted alkyl or alkoxyl group, respectively, having up to 4 carbon atoms; or

$R^1$  is selected from the group consisting of H,  $\text{NO}_2$ , CN,  $\text{OCH}_3$  or halogen or an optionally substituted alkyl or alkoxyl group respectively, having up to 4 carbon atoms, under the proviso that  $R^2$  is selected from the group consisting of an optionally substituted aryl group, an optionally substituted heteroaryl group or an optionally substituted aroyl group;

$R^3$  is selected from the group consisting of H,  $\text{NO}_2$  or halogen;

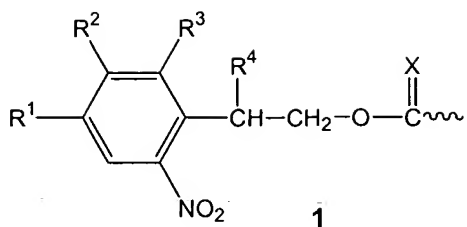
$R^4$  is selected from the group consisting of H,  $\text{OCH}_3$  or an optionally substituted alkyl group having up to 4 carbon atoms;

X is selected from oxygen or sulfur; and

Z is selected from the group consisting of a leaving group.

28. A method of claim 27 wherein Z is selected from the group of halo, imidazolyl, nitrophenoxyl, (thio)carbonate and (thio)carbamate.

29. A method for removing a photolabile protective group having the following formula:



said method comprising the step of irradiating a compound including said protective group.